Superb Electrocatalytic Activity for the Oxygen Reduction Reaction at N-doped CNT-Graphene Composite Electrodes

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Abstract

An electrocatalyst for the oxygen reduction reaction (ORR) is crucial in fuel cells and vital to the development of advanced electrochemical devices such as metal-air batteries. Replacing the expensive noble metal catalysts, which still only offer limited service life, with cheap and readily available materials for ORR applications is arguably the most important issue facing these technologies. Recently, nitrogen (N) doped carbon nano-materials have shown promise as Pt-free catalysts for ORR[1-4]. Herein, two kinds of N-doped carbon nanotube/graphene composites were developed: (i) N-CNT-N-RGO is synthesized from a pre-doped carbon nanotube and graphene; (ii) N-CNT-RGO is synthesized by first preparing a carbon nanotube/graphene oxide composite and then N-doping applied. X-ray photoelectron spectroscopy (XPS) reveals that although the overall nitrogen content of N-CNT-RGO (~ 8%) surpasses that of N-CNT-N-RGO (~5%), the ratio of graphitic N (nitrogen in graphene basal plane) to pyridinic N in N-CNT-N-RGO (0.87) is higher than that of N-CNT-RGO (0.64). Raman spectroscopy data also confirm the prevalence of nitrogen bonding contributions into the graphitic basal plane in N-CNT-N-RGO, which is the most efficient type of doping for ORR enhancement. Electrochemical tests showed that while the N-CNT-RGO exhibits high catalytic activity toward the ORR and favors a close four-electron pathway, the N-CNT-N-RGO operates at significantly higher current density and delivers superior electrocatalytic performance for the ORR with 100% selectivity for complete four electron reduction of oxygen in alkaline aqueous solution compared to a commercial Pt/C catalyst. Furthermore, the N-CNT-N-RGO demonstrates remarkable tolerance to methanol, thereby avoiding the crossover effect when operated in a direct methanol fuel cell (DMFC). It also shows highly stable performance with 93% relative current retention under 5000 continuous cycling test, which can be compared with the loss of more than 40% of the cathodic current in commercial cells (Pt/C catalyst) operated under the same conditions. The extremely high electrocatalytic activity and durability of N-CNT-N-RGO indicate that this new catalyst opens up new avenues for achieving a wide variety of cheap and commonly available metal-free catalysts for broad applications across the areas of heterogeneous catalysis, sensor, photonic catalysis, hydrogen production, and metal-air batteries.

Reference:

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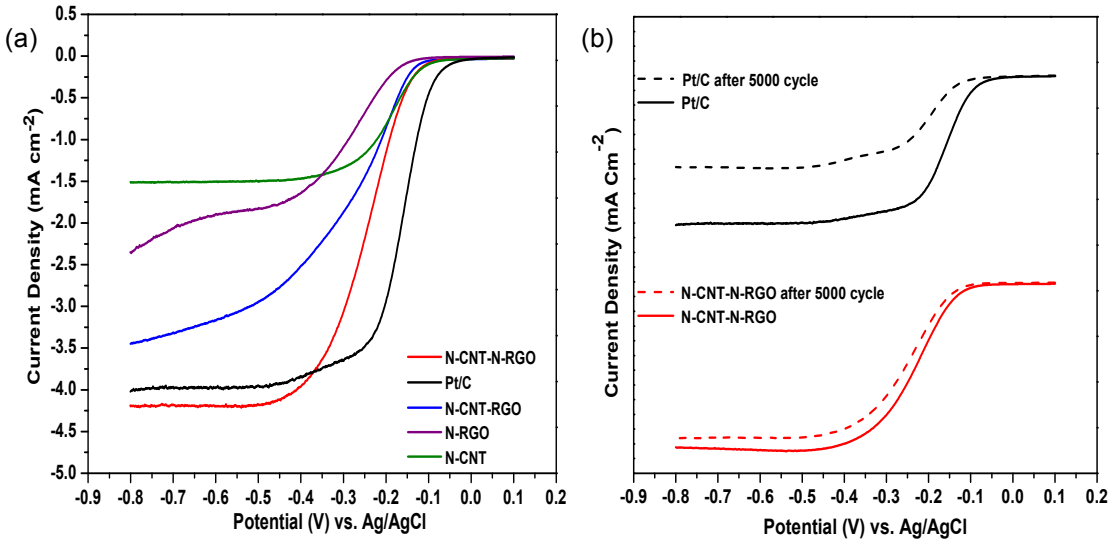

Figure1 (a) RDE voltammograms in O_2 saturated 0.1 M KOH solution at room temperature (electrode rotation speed 1600 rpm, sweep rate 10 mV/s) for the N-CNT, N-RGO, N-CNT-RGO, N-CNT-N-RGO and Pt/C. (b) Linear-scan voltammetry (LSV) of N-CNT-N-RGO and Pt/C in O_2 saturated 0.1 M KOH, before (solid line) and after (dash line) a continuous potentiodynamic swept for 5000 cycles at room temperature, scan rate: 10 mV/s, electrode rotating rate: 1600 rpm.